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U.S. ARMY CHEMICAL AND BIOLOGICAL DEFENSE COMMAND

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# LABORATORY-SCALE PRESSURE-SWING ADSORPTION PARAMETRIC STUDY: R113 ON BPL CARBON



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The U.S. Army Edgewood Research, Development and Engineering Center is investigating the pressure-swing adsorption (PSA) as a potential advanced technology approach for regenerable collective protection in military vehicles required to operate in chemical/biological warfare theaters. Experiments to test the filtration performance of a laboratory-scale PSA system have been performed by adding 1,1,2-trifluoro-1,2,2-trichloroethane (R113) to feed air-stream and monitoring the purge- and product-stream, R113 concentrations, as the challenge proceeds. In addition, in-bed probes have been utilized to monitor the R113 concentracion at 5 cm intervals along the length of the PSA bed during each experiment. The data resulting from these experiments have been used to derive PSA performance-prediction models that will assist in the design and validation of PSA-based collective protection systems for various military applications.

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PREFACE

The work described in this report was authorized under Project No. 1O162622A553, CB Defense/General Investigations. This work was started in October 1992 and completed in September 1993.

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CONTENTS

LIST OF FIGURES AND TABLES

Figures



Table

# LABORATORY-SCALE PRESSURE-SWING ADSORPTION PARAMETRIC STUDY: R113 ON BPL CARBON

## 1. INTRODUCTION

Pressure-swing adsorption (PSA) is a well-known industrial separation process used to dry air streams or separate air into its components. The PSA works most commonly by using two or more adsorbent-loaded filtration beds, one of which receives the pressurized feed stream and removes the contamination by adsorption. The purified product air stream is then expanded to near-ambient pressure and split into two streams; one is used for the application and the other is used to back-flush the off-stream adsorbent bed to remove contamination that had accumulated in previous filtration steps. After a preselected amount of time, valves are redirected so that the beds swap roles. The PSA systems often operate using four discrete steps; pressurization, feed, depressurization, and purge. However, other cycle types are possible. For example, a two-step PSA cycle combines the pressurization and feed steps and the depressurization and purge steps of a four-step cycle. Many variables are available to control the PSA operation, including feed-stream pressure, temperature, purge-to-product ratio, cycle time, total flow rate, adsorbent bed medium, bed geometry, and PSA cycle type (two-step, four-step, etc.)

The PSA takes advantage of the differences in adsorption capacities (rate), or in some cases, adsorption rates of the gaseous components to be separated on the adsorption medium. These differences in adsorption capacity can be enhanced by increasing the pressure of the feed stream.

The PSA system is under investigation as a potential advanced technology approach for regenerable collective protection (CP) subsystems in such various military applications as armored vehicles and helicopters, which are required to operate in potential chemical/biological warfare environments. It is not economically feasible to develop a PSA-based CP subsystem for any vehicle without developing a generic PSA filtration performance capability that can take into account all of the operational and environmental parameters. Neither is it a smart approach because even for a single application the constraints of that application can (and do) change during the system development process. Multiple applications with differing system constraints, power, volume, weight, etc., are under development by the military and will require a different CP subsystem design. Moreover, nonmilitary applications of the PSA technology that may benefit by developing performance prediction are also possible. Ultimately, the CP subsystem for each military CP application must undergo validation testing using a test article that closely approximates the production item. The ongoing Performance-Prediction Model Development Program at the U.S. Army Edgewood Research, Development and Engineering Center (ERDEC) is crucial in the design and validation of such CP subsystems.

This report details the results and implications of eight experiments in which 1,1,2-trifluoro-1,2,2-trichloroethane (R113) in the air

was challenged to a laboratory-scale PSA test system using BPL carbon as the adsorption medium. R113 is of interest as an adsorption simulant for the class of compounds that is moderately volatile, nonreactive, and has very low water solubility. The current effort at ERDEC is confined to two adsorbents; 13X molecular sieve and BPL carbon. Several simulants and toxic chemicals will also be tested. The results of those tests will be presented in future ERDEC reports.

Because of the large number of parameters that are possible in operating a PSA system, base-case conditions were established and variations from those conditions were examined. The development of a preliminary PSA performance prediction math model has been reported.* Comparison of experimental PSA lab-scale performance data to model predictions, including in-bed concentration profiles with time, will be described in future ERDEC reporting.

## 2. EXPERIMENTAL PROCEDURES

The lab-scale PSA operation methodology, experimental system, and associated data-acquisition system, to include the automated in-bed temperature and contaminant-concentration sampling system, were developed in-house by ERDEC and were described in detail in another ERDEC report.* Briefly, the test system is scaled so that the linear flow rate inside the PSA beds approximates that expected for such a military application as an armored vehicle, which may require as much as 15 lb per min (lb/min) of product air. The volumetric flow rate in the lab-scale experimental system was 1 cubic feet per minute (cfm) at the base-case condition. "Zero air" was generated using an oil-free compressor equipped with a refrigerated dryer. The pressurized feed air was further purified by passage through a Ballston (Lexington, MA) PSA air dryer prior to being fed to the PSA test system. Refrigerant-grade R113 (Matheson, Rutherford, NJ) was used "as received." It should be noted that distilled water and R113 could be added to the feed downstream of the air dryer by feeding the respective liquids at a controlled rate into an evaporation tower located in the feed stream.

The parameters investigated in this study included pressure ratio, purge-to-product ratio, and cycle time. The data measured included feed, purge, and product stream concentrations as well as vapor-phase R113 concentrations inside one of the PSA beds at four axial locations spaced by 5 cm; 5, 10, 15, and 20 cm from the bed feed inlet. As described in another ERDEC report,** the automated analytical system captures up to six samples

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*Mahle, J.J., Buettner, L.C., Friday, D.K., and Levan, M.D., Preliminary Pressure Swing Adsorption Math Modeling for Air Purification in Support of Armored Vehicle Applications, ERDEC-TR-082, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, July 1994, UNCLASSIFIED Report.

**Buettner, L.C. et al., Automated Adsorption Equilibrium Apparatus, ERDEC-TR-194, U.S. Army Edgewood Research, Development and Engineering Center, Aberdeen Proving Ground, MD, August 1994, UNCLASSIFIED Report.

simultaneously, usually during the feed step. The samples were isolated and sequentially fed to the analytical instrumentation; in this case, a Hewlett-Packard (Rockville, MD) Model 5890 gas chromatograph. The analysis time for each series of samples was 35-45 min. Once the sample set was measured, the cycle was repeated for the next set of samples. The data generated in this fashion resembles single-pass break-through curves, except each in-bed probe approaches a concentration limit that is less than the feed concentration. Also, the concentration limit decreases as the bed depth increases.

The PSA beds were packed using standard drop-tube methodology, followed by tapping the bed housing to promote settling of the adsorbent material. The volume and mass of each of the packed beds were measured, and the density variation from-bed-to-bed was <1%.

## 3. RESULTS

The Table in this report lists the parameters that were investigated and their values for each of the eight experiments. The base-case experiment was performed twice with essentially identical results. Three groups of experiments were performed; 1, 2, and 3 -- to evaluate the effect of feed pressure variation; 1, 4, and 5 -- to evaluate the effect of product-to-purge split; and 1, 6, 7, and 8 -- to evaluate the effect of cycle time.

The base-case experimental results are presented in Figure 1 as a plot of measured vapor-phase concentration in the feed, product, and purge air streams as well as at four in-bed probes at axial locations of 5, 10, 15, and 20 cm from the feed inlet. The concentrations are plotted as milligrams per cubic meter ($mg/m^3$) on a logarithmic scale since the data span over three orders of magnitude. Since the cycles in the base-case experiments are 1 min, the number of cycles equals the number of minutes in all Figures, except 6, 7, and 8. The total duration of the experiment depicted in Figure 1 was approximately 96 hr (four days).

Several interesting features are observable in Figure 1. First, the breakthrough times are very long. Even though for the probe was located 5 cm from the feed inlet, the R113 concentration was not measurable for about 3 hr. For the 10-cm probe, the breakthrough occurred at nearly 15 hr into the experiment, while breakthroughs at the 15- and 20-cm ports occurred at 40 and 80 hr, respectively. Once breakthrough occurred at each of the in-bed sensors, the concentration rapidly stabilized at the respective cyclic steady-state values. These cyclic steady-state concentrations decreased in exponential fashion in the experiment shown in Figure 1, which was evident by the near-equal spacing of the concentrations on a logarithmic ordinate scale. Finally, the shape of the breakthrough curve at each succeeding axial location appeared to be less sharp than that of the preceding probe.

Figures 2 and 3 depict experiments in which the effect of feed pressure was investigated. In Figure 2, the feed pressure was reduced from 45 to 30 psig. For the experimental data in Figure 2, the breakthrough times were slightly shorter at equivalent in-bed probes locations, and the

Table. Experimental Parameters Used in Lab-Scale PSA Testing of R113 on BPL Carbon

| Experiment | Feed Pressure | Product Flow Rate | Purge Flow Rate | Cycle Time |
|---|---|---|---|---|
| 1 (Base) | 45 psig | 76 sLpm | 80 sLpm | 1 min |
| 1* | 45 psig | 75 sLpm | 75 sLpm | 1 min |
| 2 | 30 psig** | 76 sLpm | 77 sLpm | 1 min |
| 3 | 60 psig** | 74 sLpm | 76 sLpm | 1 min |
| 4 | 45 psig | 49 sLpm** | 102 sLpm** | 1 min |
| 5 | 46 psig | 100 sLpm** | 53 sLpm** | 1 min |
| 6 | 45 psig | 76 sLpm | 74 sLpm | 3 min** |
| 7 | 45 psig | 76 sLpm | 80 sLpm | 5 min** |
| 8 | 45 psig | 80 sLpm | 80 sLpm | 20 sec** |

psig - pounds per square inch gauge
sLpm - standard liters per minute
*Base case was repeated to determine system performance repeatability
**Parameters altered

steady-state concentrations were higher than those for the base-case experiment. Data shown in Figures 1 and 2 indicate that the separation was poorer during the experiment conducted in Figure 2. This was evident by the appearance of R113 in the product stream after about 63 hr and by the reduced spacing between the steady-state concentrations. Figure 3 shows the effect of increasing the feed pressure from 45 to 60 psig. In Figure 3, separating R113 from the feed stream appears to be slightly better than in the base-case experiment, although the time-to-breakthrough at equivalent bed depths is significantly longer in the 60-psig experiment.

Experiments shown in Figures 1, 4, and 5 demonstrate the effect of changing the product-to-purge ratio. During these experiments, the feed flow rate was held near 150 sLpm. In the base-case experiment (Figure 1), half the air filtered by the pressurized (feed) PSA bed was depressurized and used to purge the off-stream PSA bed. When the ratio was changed so that approximately two-thirds the filtered air was used for purge, results shown in Figure 4 were produced. In this experiment, the breakthrough at the 5-cm

Figure 1. In-bed Concentration Profiles for R113 on BPL Carbon
Base Case Conditions

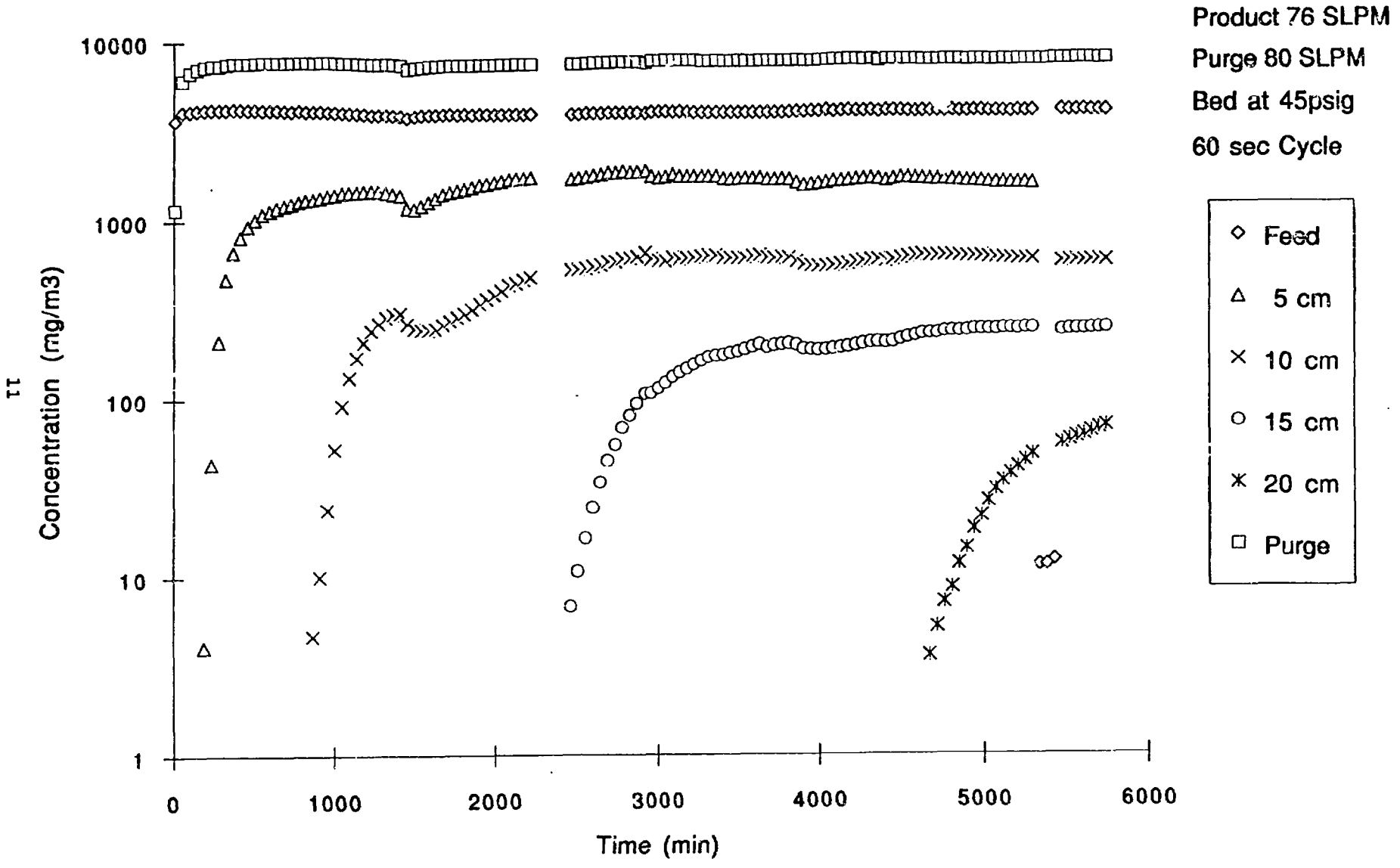
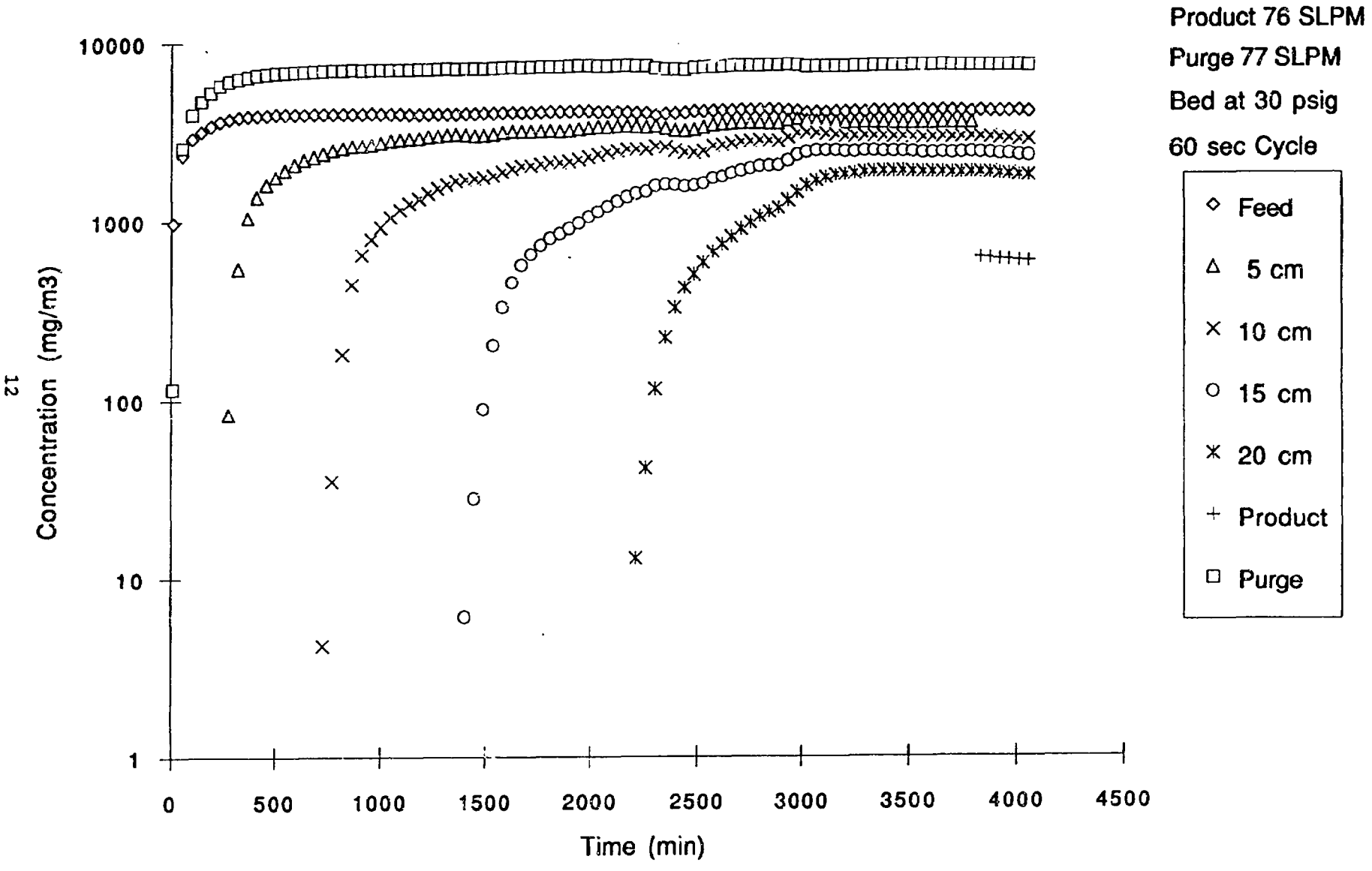
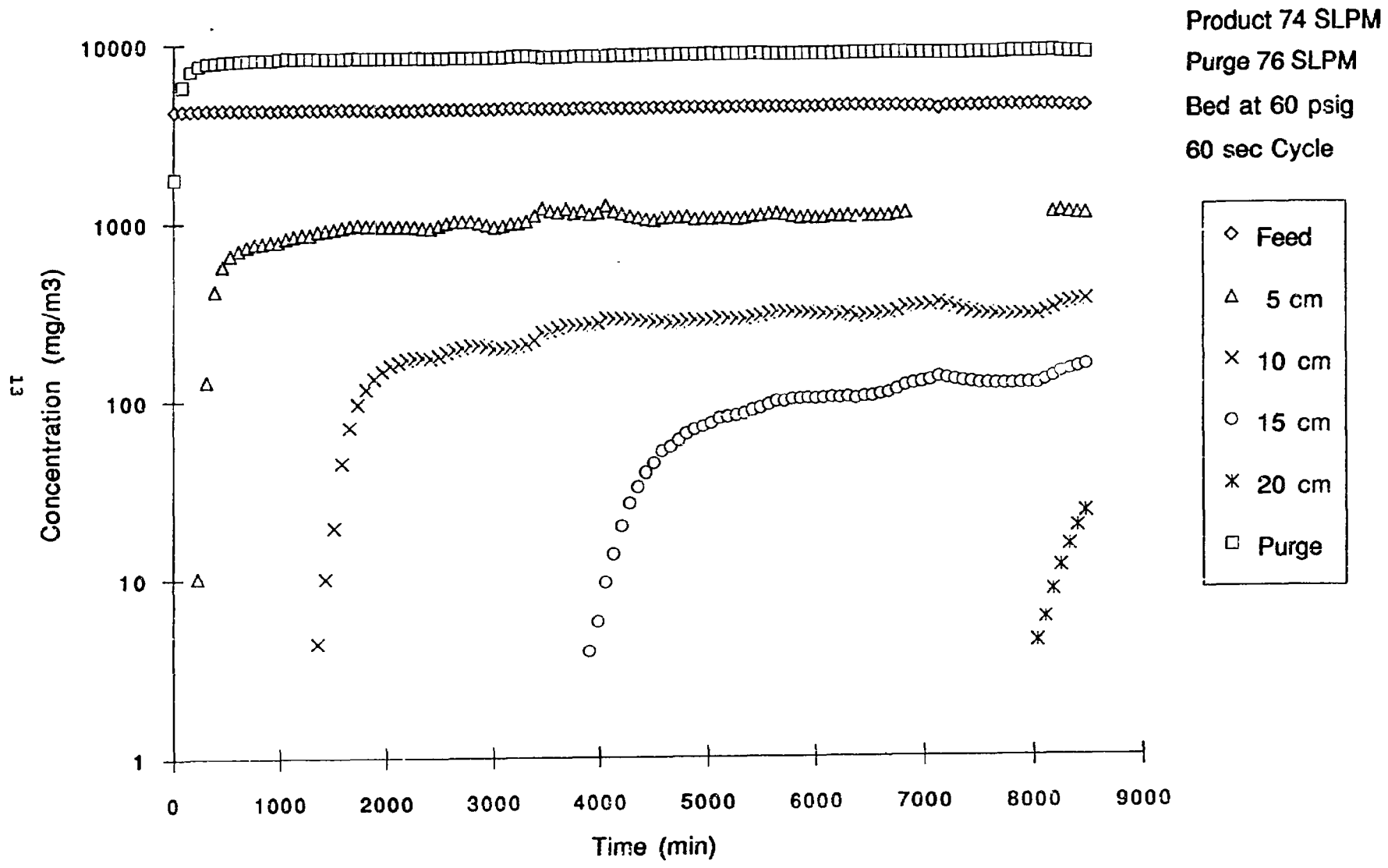


Figure 2. In-bed Concentration Profiles for R113 on BPL Carbon



## Figure 3. In-bed Concentration Profiles for R113 on BPL Carbon



## Figure 4. In-bed Concentration Profiles for R113 on BPL Carbon

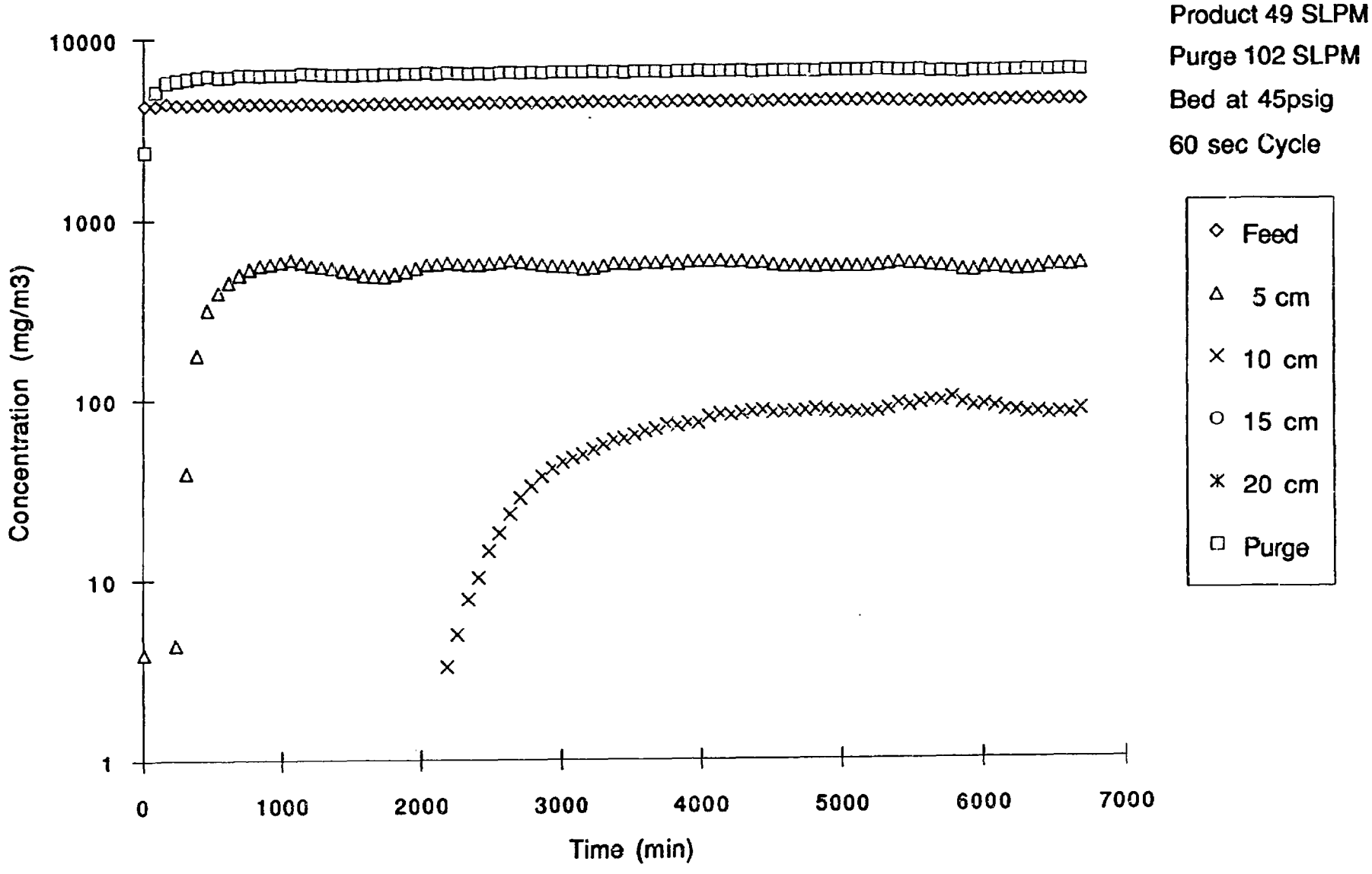
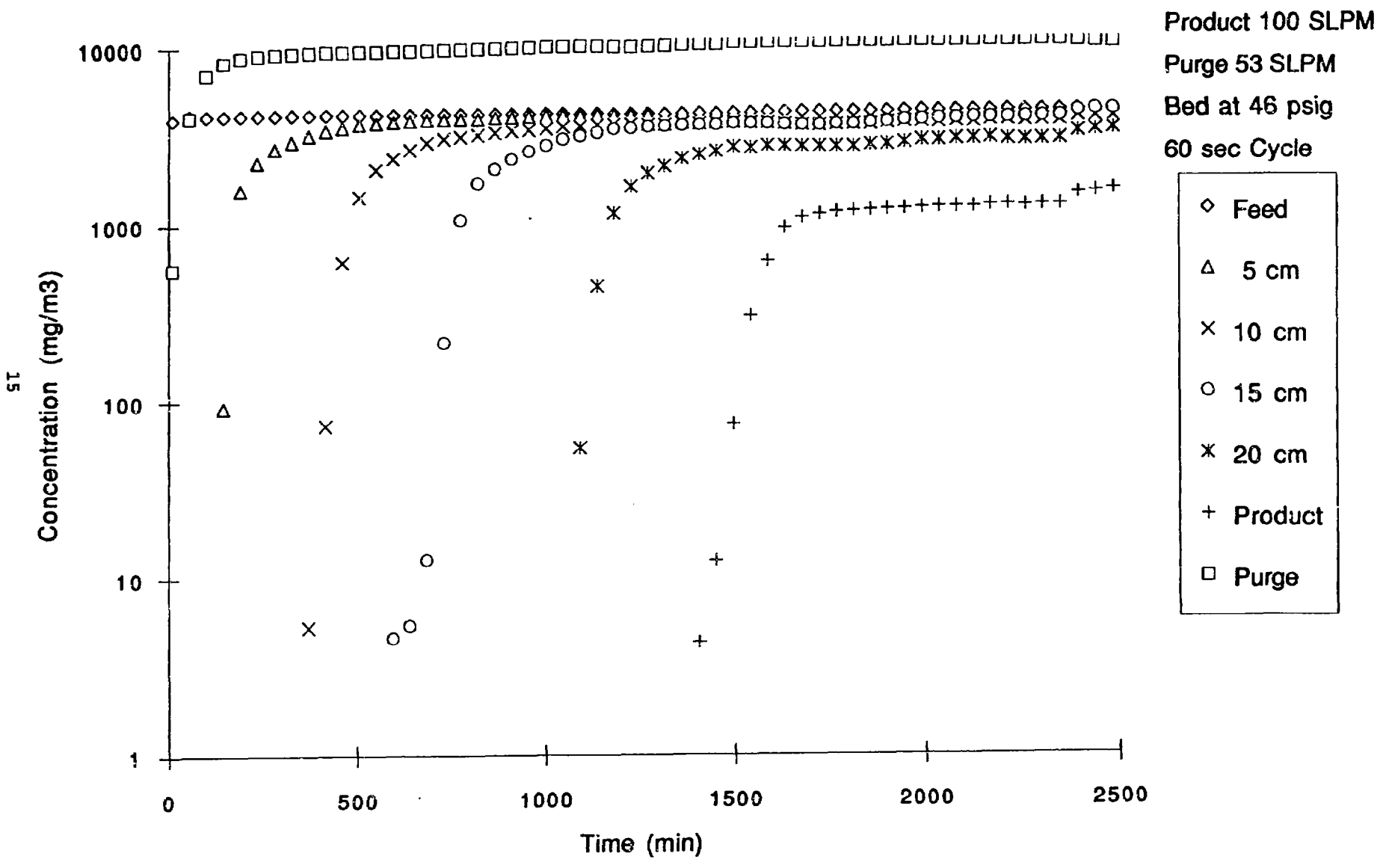


Figure 5. In-bed Concentration Profiles for R113 on BPL Carbon



probe was still rather short (200 min) but the steady-state concentration was less than half that observed in the base-case experiments. The breakthrough time at 10 cm was more than twice the breakthrough time measured in the base condition, and R113 was not seen at 15 cm after over 100 hr. Figure 5 shows the PSA performance resulting when the split was changed so that approximately one-third the filtered air was used for purge. In this case, the breakthrough times were much shorter than those for the base case, and the concentrations at steady state were higher at each probe location. The separation was much poorer, which was indicated by small spacings between steady-state concentrations; the R113 in the product stream was after about 20 hr.

Experiments shown in Figures 1, 6, 7, and 8 were performed to assess the effect of changing the cycle time. Figure 6 shows the PSA performance when the cycle time was changed to 3 min (i.e., 90 s of feed followed by 90 s of purge for each bed). The breakthrough times were shorter and the steady-state concentrations were higher at each in-bed probe position during this experiment than those in the base-case condition. When the cycle time was increased to 5 min (Figure 7), the PSA system performance deteriorated even further, which is evident by even shorter breakthrough times and higher steady-state concentrations at the in-bed sample probe positions than those in the 3-min-cycle experiment. Even with the degraded operation, breakthrough at a 5-cm bed depth was not observed until about 2 hr into this experiment. Finally, the experiment shown in Figure 8 was performed to assess the effect of running at a shorter cycle time of 20 s, (i.e., 10-s feed, 10-s purge). In this case, the PSA system performance was poorer than that in the base-case experiment. The breakthrough times were shorter [e.g., 10,000 cycles (3,333 min) at 20 cm in the 20-s-cycle-time experiment and 4,500 cycles (4,500 min) at 20 cm in the 1-min-cycle-time experiment]. In addition, the steady-state concentrations in the 20-s-cycle-time experiment were higher than those in the base-case experiment. Finally, R113 was observed in the product air stream after 16,000 cycles (5,300 min).

## 4. DISCUSSIONS

The results of all of the parametric studies clearly demonstrate the value of in-bed probes for quantitative evaluating operational parameter changes that do not show up as changes in overall system performance. For example, no contamination was detected in the product stream in Figures 1, 3, 4, 6, and 7. However, the in-bed concentration data lead to enhanced analysis of the effects of operational parameters and residual protection capacity at various conditions. Similar conclusions can be drawn for changes in feed pressure and purge-to-product split. In the latter cases, however, R113 was observed in the product streams during low-purge and low-feed pressure conditions. Parameter-induced performance effects will be discussed in the next 3 paragraphs.

Figures 1, 2, and 3 explore the effects of feed pressure on the PSA system performance. The effect of reducing the feed pressure to 30 psig was drastic in terms of steady-state performance but probably not significant in terms of protecting the product air from any sort of reasonable challenge a

Figure 6. In-bed Concentration Profiles for R113 on BPL Carbon

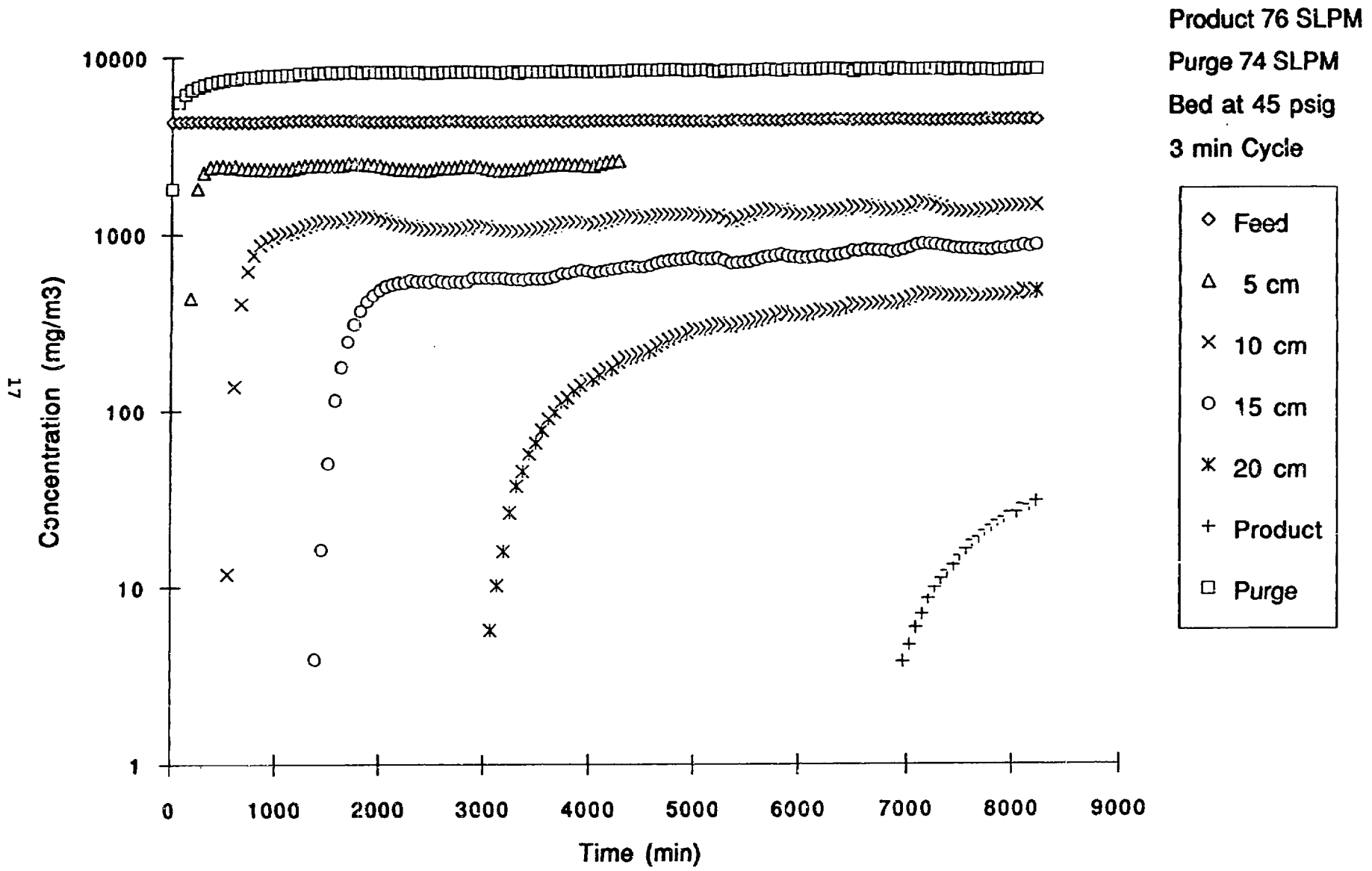
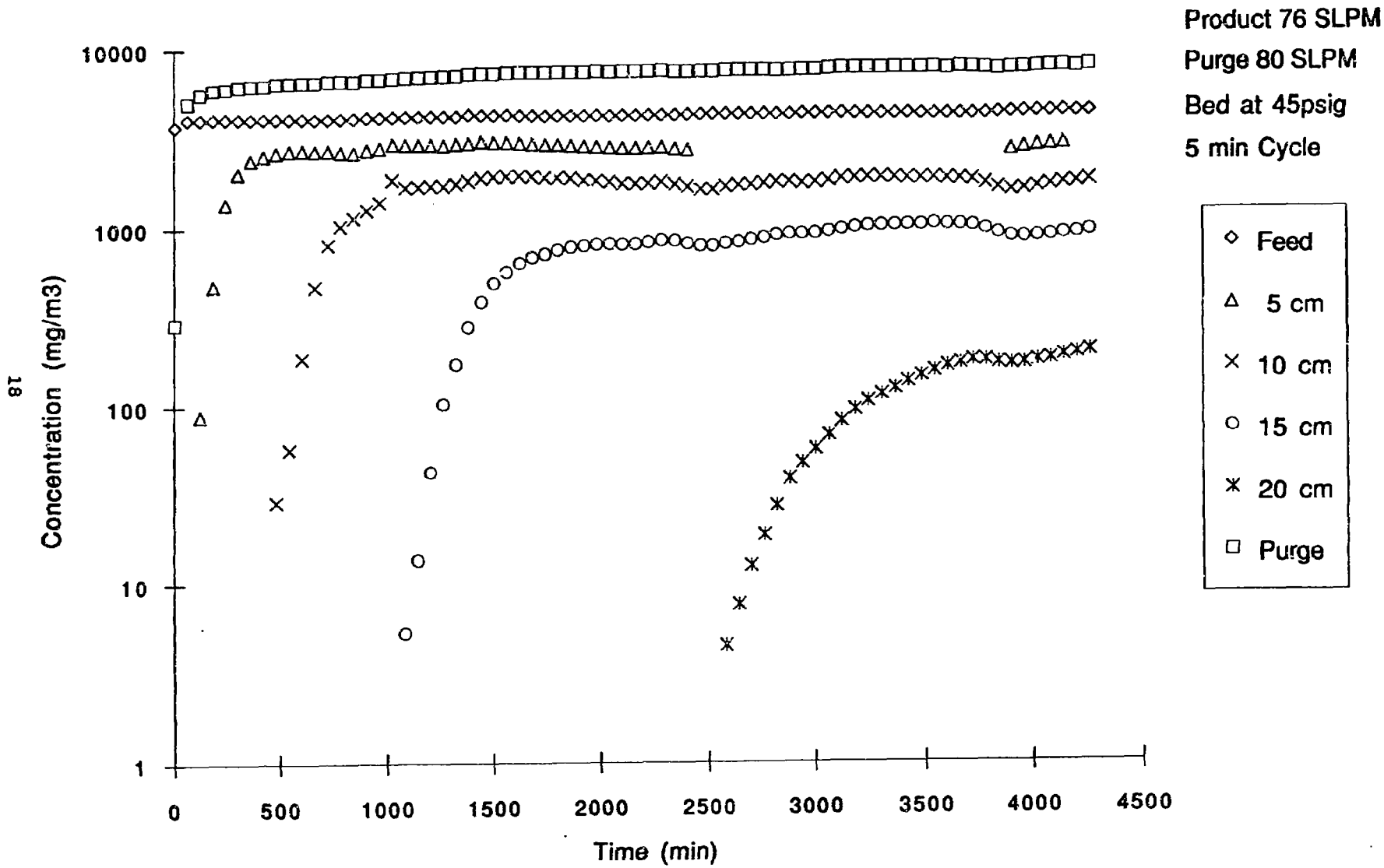
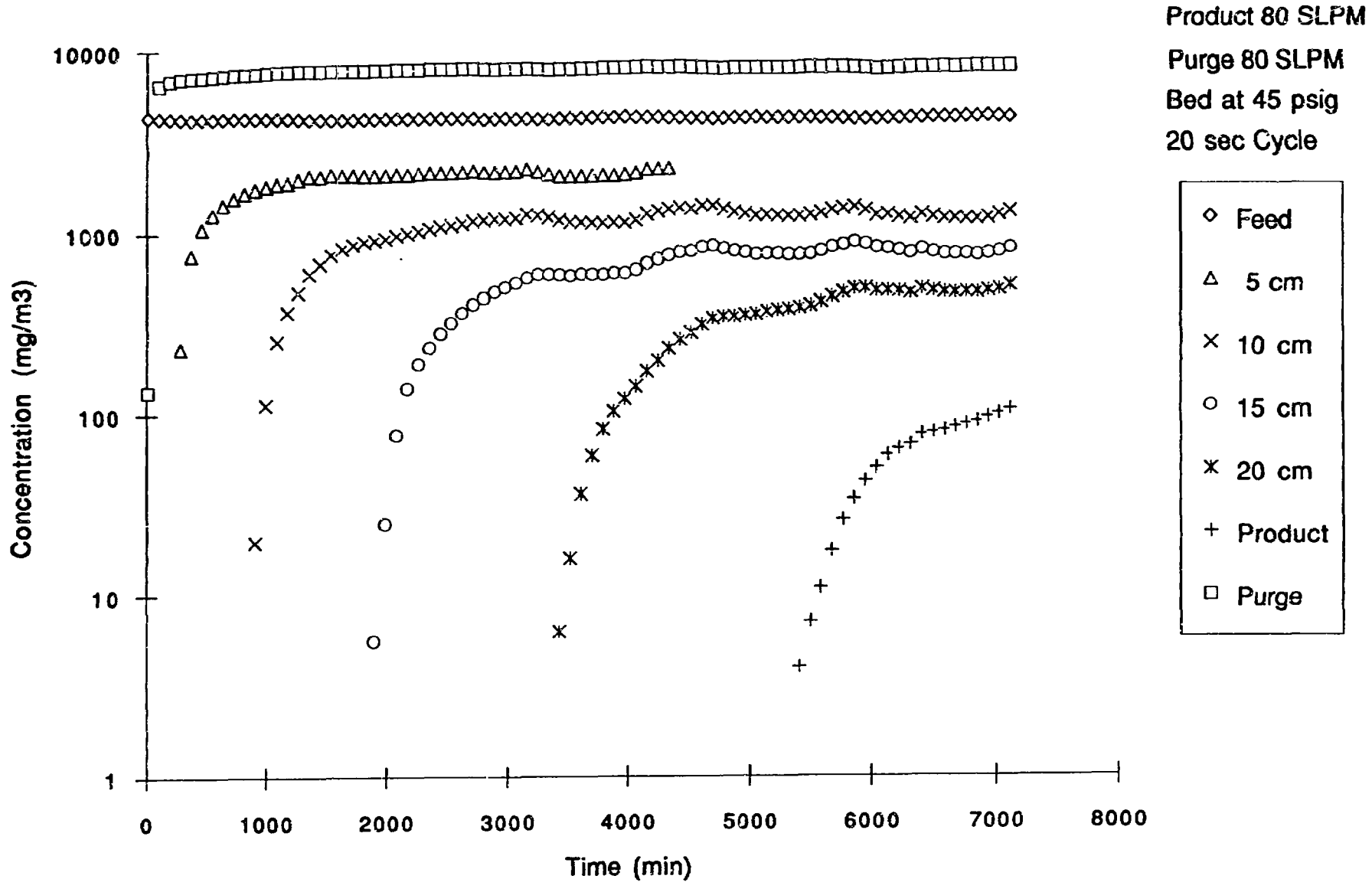


Figure 7. In-bed Concentration Profiles for R113 on BPL Carbon



## Figure 8. In-bed Concentration Profiles for R113 on BPL Carbon



PSA system might experience in the field against chemicals as volatile as R113. Even at the 5-cm bed depth, the breakthrough time was nearly 3 hr under steady challenge of 4,000 mg/m$^3$ in Experiment 2. Nevertheless, the data indicate that a system designed like the one in the current experiments will perform better at 45 psig than at 30 psig. On the other hand, little advantage is gained by operating at 60 psig rather than 45 psig in relation to long-term operations. However, there was an incremental advantage in the 60 psig system in the breakthrough time.

Figures 1, 4, and 5 explore the effects of changing the product-to-purge split on the PSA system performance. The effect of favoring the purge by a 2:1 ratio (shown in Figure 4) was to increase the breakthrough time at the 10-cm sampling port from 900 to 2,100 min. The steady-state concentrations at all sampling ports were lower in this experiment, so much so that no R113 was detected at either 15 cm or deeper into the bed in this experiment. The effect of favoring the product by a 2:1 ratio (shown in Figure 5) was to decrease the breakthrough time at the 10-cm sampling port from 900 to 350 min. The steady-state concentrations at all sampling ports were higher in this experiment, and R113 was detected in the product 1,400 min into this experiment.

Figures 1, 6, 7, and 8 demonstrate the effect of changing cycle times. Interestingly, filtration performance was found to degrade if the cycle time got either longer or shorter, both in terms of higher in-bed concentrations and shorter breakthrough times. Longer cycles will eventually lead to breakthrough by bed saturation effects, and the trends observed during the experiments shown in Figures 6 and 7 were as expected. The value associated with shorter cycle times, however, is not so simple. With short cycles, the portion of time required for pressurization and depressurization of the beds increases when compared to the feed and purge times. More importantly, the percentage of time increases in which high-concentration contaminated air is being fed to the onstream PSA bed at high flow rates. The optimum cycle time will depend on the type of cycle (two- or four-step) being used, the adsorbate being removed, and other parameters.

## 5. CONCLUSIONS

Some of the most important parameters affecting the pressure-swing adsorption (PSA) system performance include purge-to-product ratio, feed pressure, and cycle time. These parameters have been investigated on a laboratory-scale PSA system equipped with in-bed concentration probes. Performance trades and critical design information can be measured using these techniques. The effects of feed pressure and purge-to-product ratio parameters were consistent with what might be expected; however, this study shows that the qualitative trends were not simple linear dependencies. It might have been expected that the PSA separation performance would improve monotonically as the cycle time shortens. The present results are consistent with this prediction, down to the shortest cycle times tested in this work (20 s). The cycle-time effects depend on several parameters and are being investigated further.